

# A Non-Conventional Way of Developing Cement Slurry for Geothermal Well

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## ABSTRACT

The high temperatures and often aggressive brines normally found in geothermal well conditions cause rapid deterioration of the set cement and shorten dramatically the life expectancy of the wells.

In this paper we propose an unconventional way of designing cement slurries for geothermal wells.

This method requires the addition of specific solids at very high concentration. Therefore the physics of optimizing the packing between the different components of the material had to be mastered. This already allowed obtaining slurries with significantly better properties (permeability, compressive strength) than conventional slurries.

The extensive use of thermodynamics in a second step allowed us to target the mineral phases known as stable under geothermal conditions, the chemical composition of the dry cement being then modified to reach those target phases in the set cement.

Playing with the sizes and the crystallinity of the added particles then controls the kinetics of the formation of these phases.

In this paper, we will present this methodology through some examples. Physical Properties obtained at high temperature (300°C) will be presented and correlated with mineralogical analysis.

Additionally cases where mechanical stress is also applied will be reviewed. Chemical and mechanical durability will be discussed.

## Introduction

After drilling an oil well or the like, a casing or coiled tubing is lowered into the hole and cemented over all or part of its depth. In particular, cementing prevents exchange of fluids between the different layers of formation traversed by the hole, prevents gas from rising in the annular space surrounding the casing or limits the ingress of water into the production well. Its principal purpose, of course, is to support the casing.

In the exploitation of geothermal wells, environmental conditions are much severe than in oil wells with very high

temperature and highly aggressive brine. For safety and reasons, the set cement sheath has to be durable in order to ensure its integrity and to protect the casing from corrosion and the fluids present in the different geological formations (M. *et al.*, 1988)).

In the vast majority of cases, a Portland cement is used as the hydraulic binder, a material that is essentially composed of calcium silicates and calcium aluminosilicates. In the presence of water, those mineral phases hydrate and preferentially form hydrated calcium silicate (CSH) and also portlandite ( $\text{Ca}(\text{OH})_2$ ) and aluminium sulphate. CSH is a gel, which is largely responsible for the cohesion and mechanical strength of the cement in the short to medium term.

When the temperature exceeds about 100°C, in the first few months the majority of cements lose compressive strength and become permeable. Then they regain their strength and their permeability reduces. That phenomenon, known as retrogression, is due to metamorphosis of CSH gel to a highly crystalline phase known as alpha dicalcium silicate,  $\alpha\text{-C}_2\text{S}$ , which is much more dense than CSH with a contraction in volume and an increase in the porosity of the cement. This results in disintegration of the cement, which increases in rate as porosity increases, rendering it more sensitive to chemical attack such as channeling of brine or circulation of carbon dioxide.

To avoid the phenomenon of retrogression, silica in the form of sand or silica flour is systematically added to compositions which have to withstand temperatures of more than 100°C. Adding 35% to 40% of silica (with respect to the weight of Portland cement) brings the  $\text{CaO}/\text{SiO}_2$  ratio (usually denoted C/S) to about 1.

Under those conditions, CSH then transforms at about 110°C to tobermorite  $\text{C}_5\text{S}_6\text{H}_5$ , then to xonotlite  $\text{C}_6\text{S}_6\text{H}$  if the temperature is raised to 150°C. Those phases ensure the stability of the cement at high temperature, in the absence of brine. Those minerals are in themselves very strong but they have slightly different apparent densities, which destabilizes the cement. Further, near 250°C, a new mineralogical phase, truscottite ( $\text{C}_7\text{S}_{12}\text{H}_3$ ) forms, which further embrittles the cement and increases its permeability (Nelson, 1990). The degradation mechanisms described above are certainly not exhaustive, and

least because the roles of other oxides present in the Portland cement, in particular alumina and ferrites, have been ignored, but they suffice to demonstrate the complexity of the phenomena occurring, without even considering the reaction products between the cement matrix and brines. In nature, in a geological medium, cement is thus meta-stable. In contact with brine, its mineralogical repertoire is modified by ion exchanges, which modify its physical qualities.

The problems of cement disintegration when the temperature is raised are more severe when developing very deep wells, or injecting steam to recover highly viscous oils, or in geothermal wells to exploit geothermal energy.

In geological area, rocks of basic compositions (poor in silicium, rich in calcium) keep a low porosity and a good mechanical resistance during weathering and are considered in this study as good natural analogues to conventional cements (Barlet *et al.*, 1998). Anorthite, grossular, prehnite and zeolite occur in basic rocks of magmatic origin, transformed in metamorphic or hydrothermal conditions.

In pioneer work, Roy *et al.*, (1979) have shown that anorthite will behave as a cementitious material (Roy, D.M. *et al.*, 1979). However, the optimization of the conventional slurry properties has been proven to be very difficult.

The aim of this study is to develop novel formulations suitable for cementing oil, gas, geothermal wells or the like, based on a Portland and alumina type cement tending to form mineral phases such that the properties of the cement matrix, in particular regarding compressive strength, do not degrade in practice under the effect of a rise in temperature and pressure (250°C-300°C; 20 MPa) and/or chemical attack (brines).

This study describes a new method to promote easily anorthite formation during the hydration of operating slurry by adding specific modifiers. Moreover, it is shown that anorthite characterized by solid solutions exhibits the best adaptation to severe chemical environment.

## Experimental Procedure

### Materials

In order to promote the formation of anorthite, large amount of specific modifiers have to be added to the cement powder. At the same time, the final slurry density has to be as low as possible (1.4 to 1.5 sg) (due to the low fracture gradients generally experienced in geothermal wells) while maximizing the solid fraction of the slurry to discuss the permeability and increase the compressive strength.

To achieve this, the physics of optimizing the packing between the different components of the material has to be mastered. The particle size distribution of each component has to be optimum (Figure 1 illustrates an example of a trimodal blend for which the packing has been optimizing).

This technique allows the use of large amounts of solids while making the slurry still easily pumpable.

Class G cement was used as the hydraulic binder. Cenospheres of very low density (0.7 to 0.8 sg) were added to decrease the slurry density.

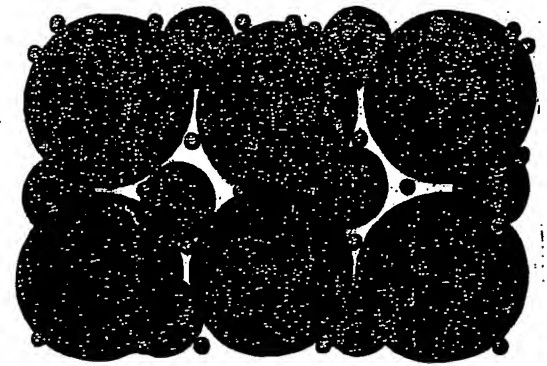


Figure 1. Trimodal blend with optimum particle sizes.

Silica flour and aluminum modifiers are the others components of the blend.

Apart from the cement for which the particle size is controlled by the manufacturer, particle size of cenospheres, silica and aluminum modifiers were carefully selected in order to achieve maximum packing of the blend.

The size and the crystallinity of the different blend components allow controlling the kinetics of anorthite formation.

Fresh water was used to prepare all the slurries.

### Blends

Different blends were prepared. The compositions of the blends in the quaternary system (CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O) are shown in Figure 2.

Table 1 summarizes the physical properties of the blends and slurries.

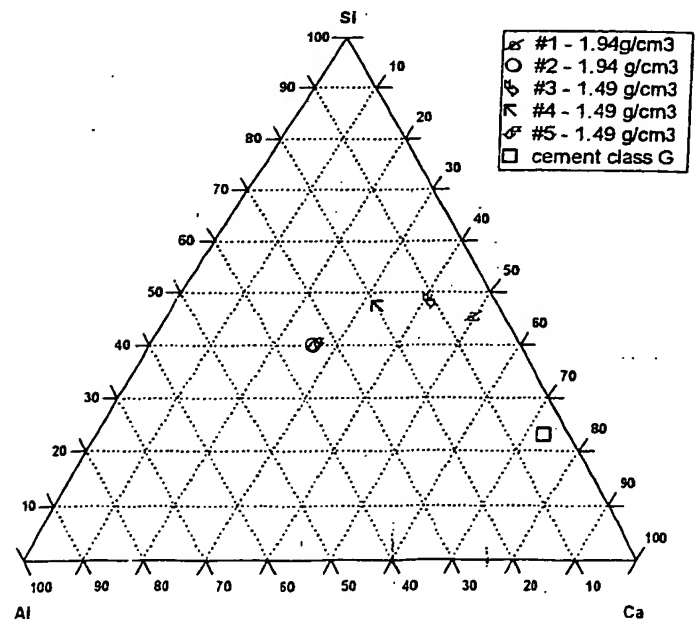


Figure 2. Projection of cement compositions, 1,2,3,4,5 in the quaternary system CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O. (CASH).

Table 1. Properties of the slurries of new cement.

No slurry	#3	#4	#5	#2	#1
Density (g.cm <sup>-3</sup> )	1.4	1.49	1.49	1.94	1.89
W/C ratio	1.3	0.58	0.81	1.07	0.69
Solids Volume Fraction	0.40	0.59	0.59	0.43	0.42
Free Water	0	0	0	0	0
Blend	Cement Silica flour Cenospheres	Cement Silica flour Cenospheres Aluminum modifier	Cement Silica flour Cenospheres Aluminum modifier	Cement Silica flour Aluminum modifier	Cement Silica flour
Plastic viscosity (cP)/Yield value after mixing (lbs/100 sqft)	33/6	257/29	109/9	53/21	149/11
Plastic viscosity (cP)/Yield value after 20 min conditioning (lbs/100 sqft)	16/13	109/3	54/6	30/15	85/7
Reading on FANN mod.35SA viscosimeter (R1-B1-F1)					
Gel at 10 min	11	21	15	35	4
Thickening Time (hours)	6:00	4:54	4:16	5:09	4:52
Transit Time	0:06	0:02	0:05	0:15	0:05
Compressive Strength after 24 hours at 400°F					
50 psi	3:43	4:40	4:34	6:02	-
500 psi	11:55	5:53	6:15	6:55	4:29
24:00	680	2100	1480	2420	6000

All slurry properties have been measured as per API specifications (procedure (API Recommended Practice for testing Oil-Well Cements and cement Additives (1990) API Spec.10 Fifth Edition (07.01.1990)).

## Slurries

The slurries are mixed following the API procedure. Mixing is done in a Waring Blender. All solid components are dry blended before being added into the water containing the liquid additives.

## Curing Conditions

### Curing 1

Once the slurry design has been optimized, samples are prepared for curing by pouring the mixed slurry into a 5cm x 5cm x 5cm steel molds. Five cubes are prepared for each formulation.

The molds containing the slurries are cured for three days at 300°C over 21 MPa in a standard oil well cement-curing chamber in water. The temperature is gradually increased to 300°C

over a 6-8 hour heat up period, to minimize possible cracking of the samples due to thermal expansion.

The temperature is maintained at 300°C and 21 MPa for 28 days, after which the system is allowed to cool down to room temperature.

### Curing 2

The cured set cement samples obtained after 28 days exposure at 300°C, are drilled in 2.5 x 5 cm cores. These set samples are exposed to the production brine at 300°C over 21 MPa in the high pressure – high temperature geothermal reactor (Figure 3) for 28 days.

The brine is regularly (each 3 days) changed to keep the solution saturated and to simulate as close as possible actual well conditions, where the brine is an "open system". The heating rate to reach 300°C is 6°C/min.

Samples are then removed, kept under water at room temperature before being tested for the following physical property measurements:

- Uniaxial compressive strength performed on 2.5 x 5 cm cores in using a compressive machine
- Water Permeability



Figure 3. Geothermal reactor.

Mineralogical examination is carried out by x-ray powder diffraction using CuK $\alpha$  radiation. Scanning Electron Microscope images are used to describe morphologies of reaction products and to complete the XRD analysis.

## Brines

Two types of brines have been used to simulate the chemical attack.

Table 2 shows the chemical composition of the production brine circulated in a Japanese geothermal well at 1300 meters with a production temperature around 300°C.

The pH of this brine is 2.6.

Table 2. Chemical composition of the production brine (Brine1).

Ions	mg/l
Na	3120
K	810
Ca	1460
Mg	270
Cl	9570
SO4	201
SiO2	144
Fe	648

Table 3 shows the composition of a California brine.

Table 3. Chemical composition of the field brine (Brine 2).

Ions	g/l
NaCl	200
KCl	23
CaCl2	63
MgCl2.6H2O	1

## Results

### Mineralogical Examination

The results of the mineralogical composition of the different samples before and after brine attack are presented in Table 4.

Figure 4 presents in the same quaternary system CASH than in Figure 2, the blend compositions from Table 1 and the different phases known as stable at 300°C.

Two areas can be defined:

- Area 1, outside the two joins Epidote-pectolite and Prehnite-pectolite
- Area 2 near or inside these two joins where the formation of xonotlite can be avoided or limited.

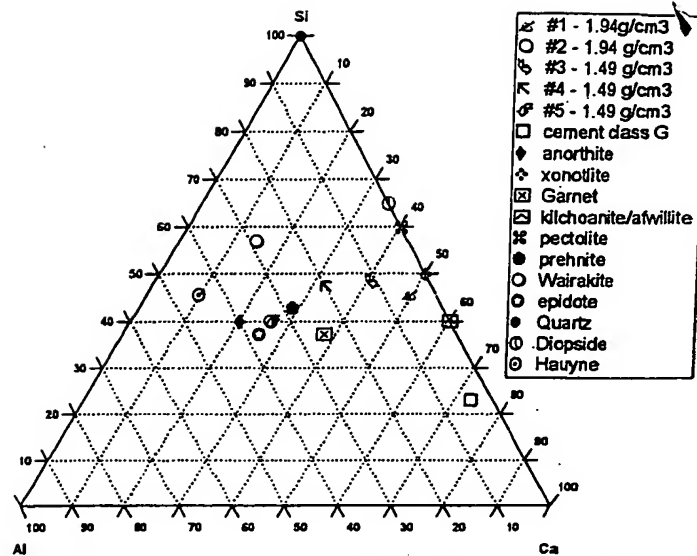


Figure 4. Quaternary system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O showing the main minerals occurred in basic-rocks after a hydrothermal alteration. Potential hydrothermal cement compositions are plotted.

In area 1, two compositions have been tested, #1 and #3 with 1.94 and 1.49 g/cm<sup>3</sup> densities respectively.

The phase responsible for the cementing properties within this region is mainly xonotlite.

With the low-density cement composition (#3), anorthite in a fairly good amount is well detected. Its composition contains more alumina than the one at higher density.

Table 4.

Formulation Number	#3	#4	#5	#2	#1				
Density g/cm3	1.49	1.49	1.49	1.94	1.94				
	Before Brine attack	After Brine 1 attack	Before Brine attack	After Brine 1 attack	Before Brine attack	Before Brine attack	After Brine 2 attack	Before Brine attack	After Brine 2 attack
Brine 1 or 2 attack at 300°C @28days									
Xonotlite									
C <sub>6</sub> S <sub>6</sub> H	++++	++++	++	++	++	++	++	++++	++++
Anorthite									
CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	++	++	++++	-	++++	+++	++++	-	-
Anorthite,sodium,intermediate (Ca <sub>2</sub> Na)(Si,Al) <sub>4</sub> O <sub>8</sub>	-	-	-	++++	-	-	++	-	-
Albite									
NaAlSi <sub>3</sub> O <sub>8</sub>	-	-	-	+++	-	-	-	-	-
Wairakite									
CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> .2H <sub>2</sub> O	-	-	++	++	++	-	-	-	-
Prehnite (zeolithe)									
[Si <sub>3</sub> AlO <sub>10</sub> ]Ca <sub>2</sub> Al(OH) <sub>2</sub>	-	-	-	-	-	++	+	-	-
Epidote 1-2									
[Si <sub>2</sub> O <sub>7</sub> ](SiO <sub>4</sub> )(OH)Al <sub>2</sub> OCaAl <sub>2</sub>	-	-	-	-	-	++	++	-	-
Garnet									
[SiO <sub>4</sub> ] <sub>3</sub> Al <sub>2</sub> Ca <sub>3</sub>	-	-	-	-	-	-	++	-	-
Quartz									
SiO <sub>2</sub>	+	-	-	-	+	+++	-	-	-
Corundum									
μAl <sub>2</sub> O <sub>3</sub>	+	-	+	-	++	++	-	-	-

++++ Prevailing phase

+++ phase in appreciable amount

++ phase in fairly good amount

+ phase in small amount

After brine 1 attack, the set cement matrix shows deleterious signs and the water permeability after one month in the Brine 1 increases. Fine needles of xonotlite shows dissolution signs particularly on the core borders.

In area 2, the compositions #4, #5, #2 have been investigated.

The composition #2 has 1.94 g/cm<sup>3</sup> of density and has been cured in the brine 2.

Compositions #4 and #5 have a lower density, 1.49 g/cm<sup>3</sup>.

Phases responsible for the cementing properties within this area are mainly anorthite, whatever the slurry density.

For the composition #4, a high temperature calcium zeolite, wairakite well detected by XRD and SEM analysis contributes with anorthite to favourable cementitious properties at 300°C.

The composition #5, containing more alumina and less silica but having the same density, shows a mineralogical "assemblage" more complex: relic phases as silica and alumina are well detected and wairakite is less observed with SEM. This composition seems to be slower than #4.

If the slurry density is initially higher (#2), anorthite stays the main binder but prehnite, epidote are well detected. Relic phase as silica and alumina are still not completely consumed after one month at 300°C.

Wairakite is not detected. Composition #2 contains a part of silica coarser than the one added in the composition #5. That can explain a lower reactivity after one month resulting from lower water saturation in silica useful to form this phase.

After brine attack, whatever the slurry density, anorthite evolves to a sodic plagioclase member, albite that shows well the good adaptation of anorthite to chemical alteration.

## Physical Properties

The compressive strength and the water permeability of the set cement after curing without or with the brine are presented in Table 5.

Table 5. Compressive strength before and after brine attack and water permeability after brine attack for the different compositions.

Formulation Number	#3	#4	#5	#2	#1
Density g/cm <sup>3</sup>	1.49	1.49	1.49	1.94	1.94
BHST °F	300	300	300	300	300
Compressive Strength (psi) at BHST after 1 month	900	2332	800	2207	6352
Water permeability (mD)	0.66	0.16	0.2	-	-
Compressive Strength (psi) at BHST after 1 month in brine	830	2500	-	2300	5400
Water permeability (mD) after brine attack	2.81	0.26	-	-	-

One should notice that even though the value of the compressive strength is lower for blend 2 than #1 before brine attack, after brine attack, the formulation #2 shows no decrease in the compressive strength.

If the brine is directly added as mixing water, this trend is still observed contrary to the trend obtained with the formula-

tion #1 where the compressive strength decrease of 55% initial value.

The formulation #4, at a density of 1.49 shows no variation in the compressive strength before and after brine attack only a slight increase in permeability.

The composition #5 exhibits the lower compressive strength with a chemical system not completely reacted.

## SEM Examination

Electron microscopy gives morphological information completes the chemical, physical, mechanical diffractometric data.

The set cement matrices provided from formulation #3 formulation #4 are observed and compared before and after chemical attack.

The photos 1,2,3 and 4 presents the set cement matrix obtained with the composition #4.

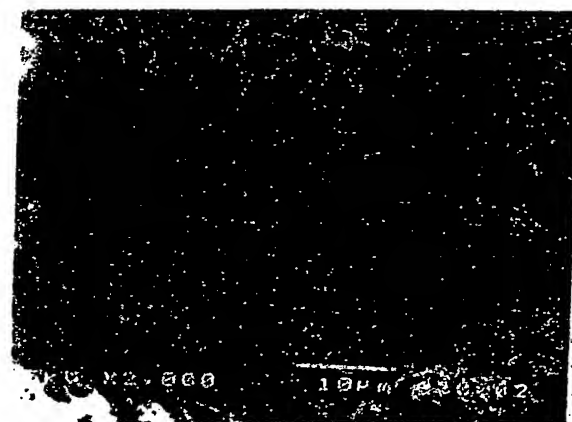
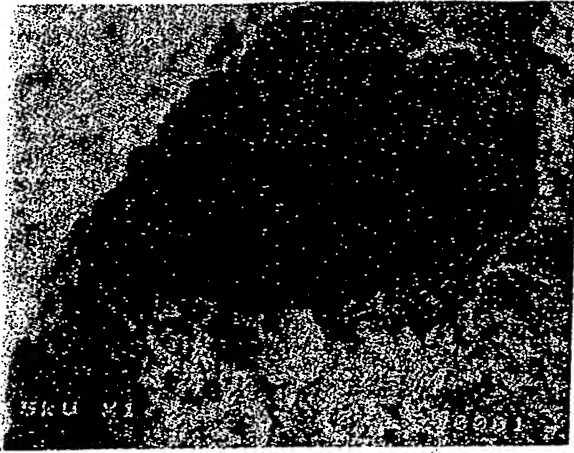


Photo 1. #4 before brine curing - X2000 - anorthite in interstitial matrix.



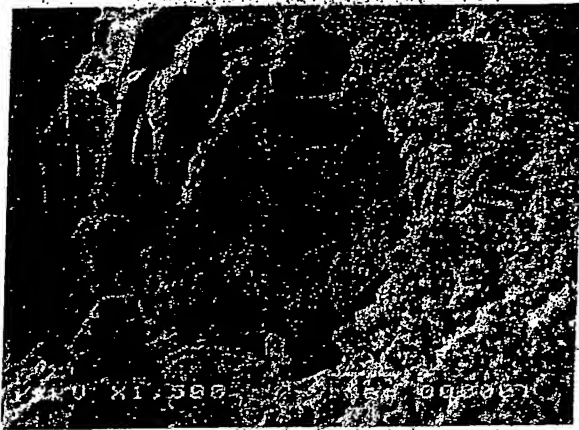
Photo 2. #4 after brine curing - X2000 - anorthite in interstitial matrix.



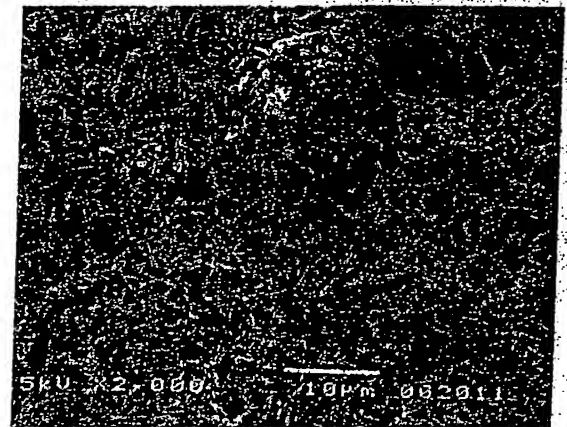
**Photo 3.** #4 before brine curing-15 kV - X1,500 – Cavity filled with anorthite.



**Photo 5.** #3 after brine curing – X2000 – sample cut inside the core – Interstitial matrix.



**Photo 4.** #4 after brine curing-15 kV - X1,500 – cavity filled with wairakite well crystallized.



**Photo 6.** #3 after brine curing – X2000 – sample from the core borders – Interstitial matrix.

Anorthite is well detected before and after brine attack in the interstitial matrix and crystallizes as interlocking platelets, which can contribute to a superior compressive strength measurement (photos 1 and 2). This phase is also met in some cavities observed in this low-density system. Again anorthite crystallizes under interlocking platelets, plugging the cavity (photo 3).

Wairakite is well observed in the interstitial matrix under cubic crystals and seems well stable after brine curing (photo 4).

The photos 5 and 6 present the set cement matrix obtained with the composition #3.

The samples have been cut in the core near the free surface and inside the core. In view of XRD analysis, xonotlite as fine needles, is the primordial hydrate. The photos 5 and 6 show the effect of brine curing through the core: in the core near the free surface, the signs of xonotlite dissolution in the interstitial matrix are more significant than inside the core. In view of the SEM observations, the increase of water permeability after brine curing can be explained: 0.66 mD and 2.8 mD before and after brine attack, respectively.

## Discussion

In view of the mechanical and durability results, the composition #4 seems to be the best candidate for geothermal applications. The permeability and the compressive strength are not affected after brine attack at 300°C.

Indeed, the results have shown that the faster anorthite forms the lower strength retrogression is observed: at 300°C, the composition #4 exhibits the higher compressive strength with a complete reaction after one month at high temperature, the composition #5 exhibits the lower compressive strength with a chemical system not completely reacted.

The fact that the original material component (cement, cenosphere, aluminum modifiers) have completely reacted can partially explain this durability. Indeed, unreacted silica, and aluminum modifiers react with brine to give secondary phases which are not necessarily stable under these conditions.

Anorthite is the calcic member of the solid solution plagioclase that is well known to be stable at high temperature and which can adapt to brine circulation by ions exchanges in its network.

Wairakite is a high temperature Ca-zeolite that is able, like all zeolite, to absorb ions in its structure that can be a good property with brine circulation. Its stability domain is well known in the system  $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  in the range 0-500°C and 0.1-10 kbar involving the phase's anorthite, grossular, prehnite and others (Frey *et al.*, 1991).

This phase does not exist in formulation #2 at higher density. A fraction of the silica in Composition #2 is coarser (silica) than the silica contained in Composition #5 (silica flower). That can explain a lower reactivity after one month resulting from lower water saturation in silica useful to form this phase. This also shows how the kinetics of the targeted phases (anorthite, wairakite) could be controlled by the particle sizes of the different components of the blend.

The resistance to carbon dioxide for those systems and especially system #4 is under investigation. The low permeability observed before and after brine curing indicate however that these systems could have a good resistance to the gas.

## Conclusions

An unconventional lightweight formulation using conventional Class G cement has been successfully designed for

temperatures up to 300°C. The set cement has shown very good indications of durability (low permeability and no strength retrogression).

The process used to design the slurry is new in the oil business. The temperature stable phases (anorthite, wairakite) are selected. Aluminum modifiers and silica oxides are added to the dry cement so that the elemental composition of the blend corresponds to the phases selected. The control of the particle size distribution and the relative amount of those minerals allow their addition at high concentration while leaving the slurry easily mixable and pumpable. The kinetics of the targeted phase formation is then controlled by playing with the crystallinity and the particle sizes of the different solids.

This process could be used whatever the targeted phase and opens the way to the design of slurries based on Class G cement for a wide range of application in the geothermal business.

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